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# A RHEED and STM study of Sb-rich AlSb and GaSb (0 0 1) surface reconstructions

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## Abstract

The structure of AlSb and GaSb (0 0 1) surfaces prepared by molecular beam epitaxy has been studied with in-situ reflection high-energy electron diffraction and scanning tunneling microscopy. Under fixed Sb<sub>4</sub> flux, two AlSb reconstructions are observed with increasing temperature (and decreasing surface Sb:Al coverage): *c*(4 × 4), as observed for InSb, GaAs, AlAs, and InAs, and (1 × 3). In contrast, GaSb reconstructions observed with increasing temperature are: (2 × 5), (1 × 5), *c*(2 × 6), and (1 × 3). Whereas the (1 × 5), *c*(2 × 6), and (1 × 3) surfaces are composed primarily of Sb dimer rows on top of an Sb-terminated surface, the (2 × 5) surface is composed of Sb dimer rows on top of two layers of Sb (i.e. the surface is terminated by three Sb layers). We speculate that GaSb is unique in forming the (*n* × 5) reconstructions due to its excellent lattice match with trigonally bonded elemental Sb.

## 1. Introduction

There is an extensive effort to develop novel high-speed and optoelectronic devices utilizing the “6.1 Å” family of III–V compound semiconductors, InAs, GaSb, and AlSb [1, 2]. Because these devices are often based on short-period heterostructures, where the interfaces constitute a significant fraction of the total heterostructure volume, the structure and stoichiometry of the growth surface during interface formation is expected to have a significant impact on the ultimate device performance [2]. The

structure of the growth front can affect the abruptness of a heterointerface in a number of ways. For example, the surface reconstructions may lead to anisotropic growth morphologies, thereby causing roughness at the heterointerface [3, 4]. In addition, the III/V stoichiometry of the reconstruction may lead to non-stoichiometric interfaces that cannot be compositionally abrupt [4, 5]. Hence, the development of smooth, abrupt interfaces requires a fundamental understanding of the structure of the III–V(0 0 1) surface reconstructions.

Given that 6.1 Å-based devices are generally grown under an As- or Sb-rich flux, the V-terminated reconstructions are the most important to understand. To date, the most intensively studied of the 6.1 Å compounds has been InAs. The As-terminated surface reconstructions of InAs(0 0 1)

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mimic those of GaAs [5–8], with As dimer-based ( $2 \times 4$ ) and  $c(4 \times 4)$  reconstructions. The Sb-terminated GaSb surface reconstructions have been less studied, although they are reported to include the Sb dimer-based “odd” reconstructions,  $(1 \times 3)$ ,  $c(2 \times 6)$ ,  $(1 \times 5)$ , and  $(2 \times 5)$ , as observed with reflection high-energy electron diffraction (RHEED) [5, 9–11]. It has been proposed that the  $(1 \times 3)$  and  $(2 \times 5)$  reconstructions are terminated with  $\frac{1}{3}$  and  $\frac{2}{5}$  layers of Sb, respectively, on a  $(1 \times 1)$  Ga plane [12, 13]. Unlike InAs and GaSb, the structure of AlSb( $0\ 0\ 1$ ) has received little attention. To our knowledge,  $(1 \times 3)$  and  $c(2 \times 6)$  [but no  $c(4 \times 4)$  or  $(n \times 5)$ ] reconstructions have been reported, and, as yet, no structural models have been proposed [5, 10, 11, 14]. In addition to the technological applications of GaSb and AlSb, these materials are of interest because they are a special pair of III–V compounds having very similar lattice constants (6.095 versus 6.136 Å) but differing only by one element (a similar relationship exists for GaAs and AlAs). As such, they provide an opportunity to explore the role of elemental properties in determining surface reconstructions.

## 2. Experimental procedure

Experiments were carried out in an interconnected, multi-chamber ultrahigh vacuum (UHV) facility that includes a III–V semiconductor molecular beam epitaxy (MBE) chamber equipped with RHEED, and a surface analysis chamber equipped with a scanning tunneling microscope (STM). RHEED studies were performed on relaxed, thick films ( $> 1 \mu\text{m}$ ) of AlSb and GaSb grown on GaAs( $0\ 0\ 1$ ) substrates oriented to within  $0.1^\circ$  of  $(0\ 0\ 1)$ . Surface reconstruction transition temperatures for a fixed Sb<sub>4</sub> flux were determined by either heating or cooling the substrate in  $5^\circ\text{C}$  increments through the transition region and recording the temperature at which the RHEED pattern changed. Substrate temperatures were determined by infrared transmission thermometry and are believed to be accurate to  $10^\circ\text{C}$  [15]. STM images of AlSb reconstructions were acquired on Si-doped ( $10^{17} \text{ cm}^{-3}$ ) thick films grown on  $n^+$ -GaAs( $0\ 0\ 1$ ) substrates at  $550^\circ\text{C}$ . These films were terminated

with 10 nm of undoped AlSb grown at a reduced rate to eliminate Si contamination on the growth surface and produce large atomically well-ordered terraces. STM images of GaSb reconstructions were acquired on undoped films grown on  $p^+$ -GaSb( $0\ 0\ 1$ ) substrates at  $500^\circ\text{C}$  with frequent interrupts. STM samples were mounted on a custom-designed sample holder that mounts onto both a standard 5 cm diameter MBE sample block and the stage of a custom-modified commercial STM [16]. All STM images are displayed in gray scale and are uncorrected for thermal drift.

## 3. Results

The structural transitions between various Sb-rich surface reconstructions as observed by RHEED for AlSb( $0\ 0\ 1$ ) and GaSb( $0\ 0\ 1$ ) as a function of Sb<sub>4</sub> flux and substrate temperature are shown in Fig. 1. Both AlSb and GaSb exhibit a  $(1 \times 3)$  RHEED pattern at high substrate temperatures. At lower temperatures, however, the surface reconstructions for these systems differ. We find that AlSb transitions to a  $c(4 \times 4)$  structure, similar

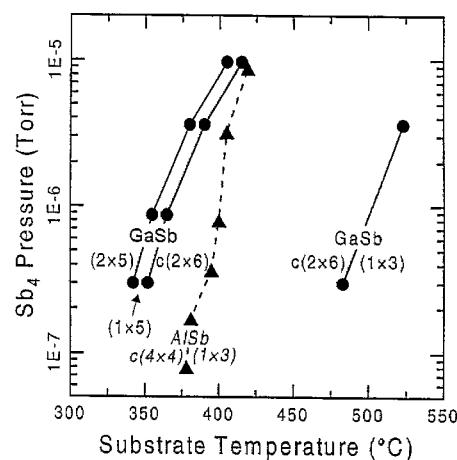


Fig. 1. Substrate reconstruction transition temperatures for AlSb and GaSb ( $0\ 0\ 1$ ) surfaces as a function of incident Sb<sub>4</sub> beam equivalent pressure as observed with RHEED. The transitions for AlSb are indicated by triangles and those for GaSb by circles. The lines are drawn as guide to the eye. A pressure of  $2.0 \times 10^{-6}$  Torr corresponds to an Sb deposition rate of  $\sim 1$  layer per second.

to the anion-terminated (0 0 1) surfaces of InSb, GaAs, AlAs, and InAs. Unlike AlSb, GaSb undergoes multiple reconstruction transitions with decreasing temperature: first from (1 × 3) to  $c(2 \times 6)$ , then to (1 × 5), and finally to (2 × 5). At still lower temperatures and/or higher Sb fluxes (not shown in Fig. 1) both AlSb and GaSb transition to three-dimensional, elemental Sb growth.

A high-resolution STM image of an AlSb(0 0 1)-(1 × 3) surface is shown in Fig. 2a. This surface appears to have a structure similar to what we and

others [12] observe for GaSb(0 0 1)-(1 × 3). The model proposed for this reconstruction consists of a (1 × 1) plane of Sb with rows of Sb dimers on top, with the dimer rows spaced  $3a_0$  apart [ $a_0$  is defined as the size of a (1 × 1) surface unit cell, 4.34 Å on AlSb]. The total Sb surface coverage for this model is  $1\frac{2}{3}$  layers [12]. We attribute the zigzag nature of the rows and quasi-periodic kinking along the rows to buckling-like displacements of the dimers, which give the surface a more complicated structure than apparent from the observed diffraction patterns. An

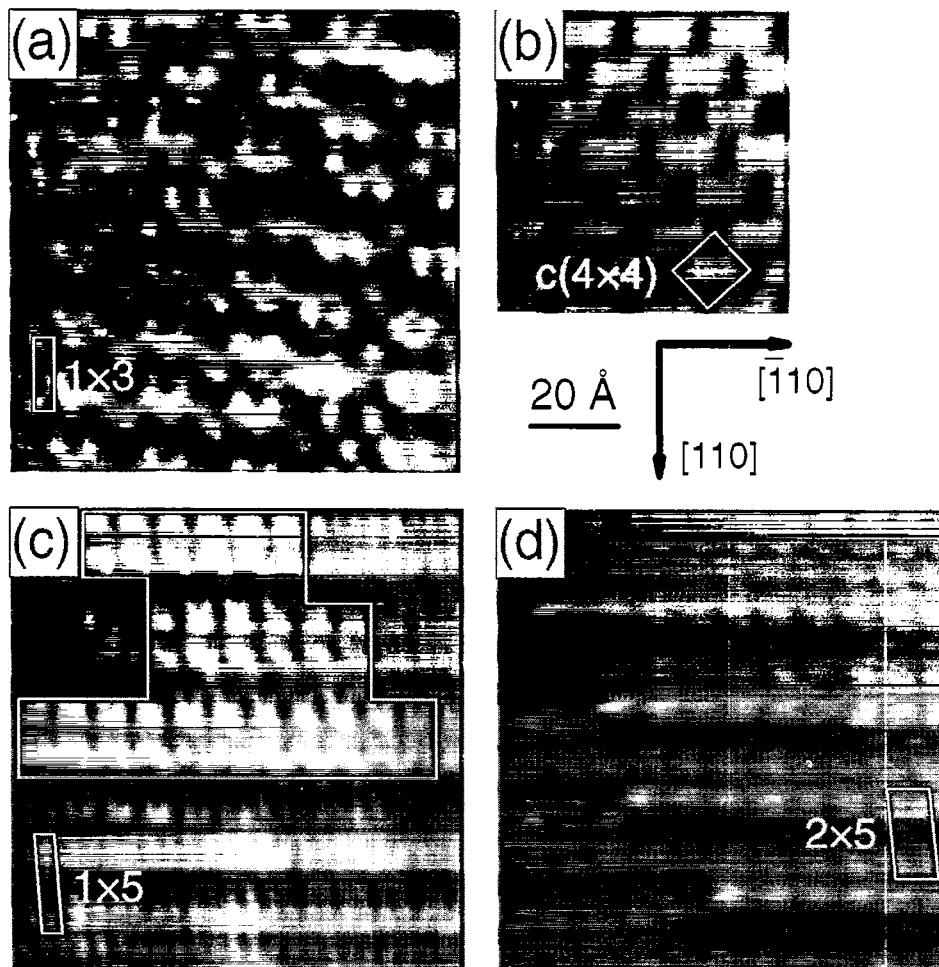


Fig. 2. Gray-scale STM images of AlSb and GaSb (0 0 1) surfaces; (a) AlSb(0 0 1)-(1 × 3), empty electronic states (3.0 V, 0.1 nA); (b) AlSb(0 0 1)- $c(4 \times 4)$ , filled states (2.6 V, 1 nA); (c) GaSb(0 0 1)-(1 × 5)/(2 × 5), filled states (2.4 V, 0.1 nA); a region with local  $c(2 \times 10)$  symmetry is outlined; (d) GaSb(0 0 1)-(2 × 5), filled states (0.4 V, 0.1 nA). Primitive unit cells are indicated. The reconstructions refer to the symmetry observed in RHEED.

STM image of a well-ordered AlSb(0 0 1)-c(4 × 4) surface is shown in Fig. 2b. This surface consists of a brick-like structure similar to that seen on both GaAs(0 0 1)-c(4 × 4) and InSb(0 0 1)-c(4 × 4) [6, 17]. This reconstruction has been shown for the other surfaces to consist of a (1 × 1) plane of V-atoms with rows of V-dimers on top; every fourth dimer is missing along each row, with the missing dimers within adjacent rows shifted  $2a_0$  apart (the total V-atom surface coverage is  $1\frac{3}{4}$  layers) [6, 17].

An image of a mixed GaSb(0 0 1)-(1 × 5) and -(2 × 5) reconstructed surface is shown in Fig. 2c (the reconstruction notation refers to the symmetry seen with RHEED). The upper-central region of this image includes a brighter patch with a (2 × 5)/c(2 × 10) reconstruction, whereas the rest of the image shows a (1 × 5) reconstruction. Although pure (1 × 5) and (2 × 5) regions were more typical, this region is shown because it allows a direct comparison between the two reconstructions. Focusing on the (1 × 5) region first, the structure consists of rows spaced  $5a_0$  apart. Each row consists of pairs of elements spaced  $a_0$  apart, with each element elongated along the [1 1 0] direction. When tunneling out of filled states closer to the Fermi level, a weak  $2a_0$  periodicity is observed between the rows (not shown). This  $2a_0$  periodicity may be either aligned or staggered from row to row, indicating that the "(1 × 5)" surface is actually a mixed (2 × 5)/c(2 × 10) reconstruction. A model for this surface reconstruction is shown in Fig. 3a, consisting of a full plane of Sb with two adjacent rows of Sb dimers on top. Between the rows are rotated Sb dimers in the second layer, which may or may not be aligned across the rows [18]. The total Sb surface coverage is  $1\frac{4}{5}$  layers. (Note that this structure is a simple extension of that proposed for the c(2 × 6) reconstruction [13], which consists of *single* Sb-dimer rows in the top layer separated by rotated second layer dimers.)

The (2 × 5) structures within Fig. 2c appear topographically higher than the (1 × 5), suggesting that there are additional Sb atoms on top. In addition, the periodic structures within the (2 × 5) rows are elongated at right angles to the dimers in the (1 × 5). These features are most simply explained by an additional layer of Sb-dimers adsorbed atop the (1 × 5) dimer rows [breaking the (1 × 5) dimer

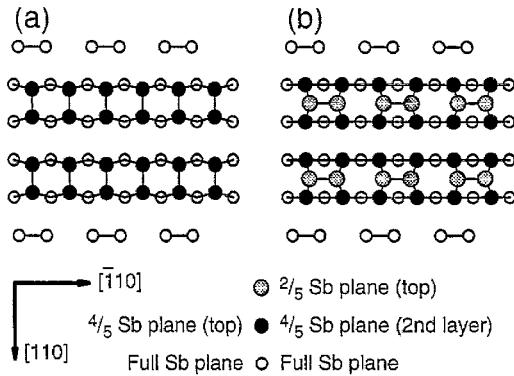


Fig. 3. Proposed structural models for GaSb surface reconstructions observed in RHEED as (a) (1 × 5), and (b) (2 × 5). The Sb planes are assumed to be separated by  $\sim 1.5 \text{ \AA}$ . Note that the Sb dimers in the second row of the "(1 × 5)" give this structure a (2 × 5) symmetry.

bonds]. The structure of the (2 × 5) reconstruction is shown more clearly in Fig. 2d. As observed in Fig. 2c, there are rows of dimer pairs along the [1 1 0] direction, with each pair of dimers spaced  $2a_0$  apart. Under the tunneling conditions for this image, elongated maxima spaced  $2a_0$  apart *between* the dominant rows are clearly visible, shifted  $\sim \frac{1}{4}$  the distance between the maxima on the main rows. A domain wall-like structure produced by rows shifted  $a_0$  along [1 1 0] is also observed in Fig. 2d. Note that shifts of  $a_0$  along [1 1 0] of the maxima on both the dominant rows and the rows in between result in areas with local c(2 × 10) and (2 × 10) symmetry.

A possible structural model for the GaSb(0 0 1)-(2 × 5) reconstruction is shown in Fig. 3b. The model is a simple extension of the (1 × 5), consisting of additional Sb dimers on top of the Sb atoms that form the dimer rows of the (1 × 5) structure, making the total Sb surface coverage  $2\frac{1}{5}$  layers. The simple structural differences between the (1 × 5) and the (2 × 5) may explain why the (1 × 5) exists for only a narrow temperature window (see Fig. 1) [9]. It is interesting to note that both of these reconstructions have more surface valence electrons than surface Sb bonds, in violation of the generally accepted "electron counting" model for III-V surface reconstructions [19].

#### 4. Discussion

A different structural model for the  $(2 \times 5)$  has been previously proposed by Sieger et al. based on RHEED and photoemission results [13]. Their model differs from ours in two respects. First, their model consists of rows of three dimers in the top-most plane, a structure inconsistent with our STM results. Furthermore, one would expect multi-layer Sb structures to be trigonally bonded [20, 21]. Whereas our model maintains a trigonally bonded environment for the top two planes of Sb, the previously proposed model only has the very top plane of Sb atoms trigonally bonded. The second difference between the two models is that their top Sb plane is bonded to a full plane of Sb, whereas our model has  $\frac{4}{5}$  of a plane of Sb as indicated by the STM images. Hence, our models differ in overall Sb coverage: the previous model has  $2\frac{2}{5}$  layers of Sb, while ours has only  $2\frac{1}{5}$  layers. This difference, however, is within the uncertainty of the published photoemission analysis [22].

Beyond understanding the details of the atomic structure of these reconstructions, one surprising observation is that GaSb does not form the  $c(4 \times 4)$  reconstruction common to all other III-Sb and III-As compounds. We believe that the unique GaSb surface reconstructions arise from a competition between adding multiple layers of Sb to the surface and the stress induced by the lattice mismatch between the resulting overlayers and the substrate. The principal source of this stress is expected to be the surface dimer bonds. For a single plane of Sb on a Ga-terminated GaSb(0 0 1) surface, an Sb dimer would result in the top Sb atoms moving from their  $(1 \times 1)$  positions ( $4.3 \text{ \AA}$  apart) to a distance closer to the natural Sb–Sb bond length ( $2.9 \text{ \AA}$ ), a 30% displacement. However, given that the lattice parameter of trigonally bonded elemental Sb ( $4.3083 \text{ \AA}$ ) [21] is nearly equal to the size of the GaSb(0 0 1) bulk-terminated unit cell ( $4.3101 \text{ \AA}$ , 0.04% larger), the strain should be significantly reduced by forming a double surface layer of Sb, enabling the subsurface layer Sb to remain in bulk-terminated GaSb-like positions. The Sb atoms within each surface dimer can then be trigonally bonded (to two atoms in the second layer plus the other dimer atom; see Fig. 3a) in a configuration

similar to that of elemental Sb. The match between these Sb structures and the GaSb substrate should be nearly perfect along the dimer row direction, resulting in dimer rows with very low strain along  $[\bar{1} \ 1 \ 0]$  that should act as an excellent template for another layer of (rotated) Sb dimers (Fig. 3b).

We speculate that AlSb(0 0 1) does not form the  $(n \times 5)$  reconstructions due to the higher stress that continuous dimer rows would induce on this surface. AlSb has a slightly larger lattice mismatch with bulk Sb (0.70%), leading to more strained surface bonds. Furthermore, the stress associated with these strains will be proportionately greater because AlSb is stiffer than GaSb (for the same displacement, it takes 7% more energy to stretch Al–Sb bonds than Ga–Sb bonds) [23]. This stress may be reduced by periodically removing some of the Sb dimers along each row and allowing for local relaxation, i.e. forming the  $c(4 \times 4)$  structure [24].

#### 5. Conclusions

We have studied the structure of AlSb and GaSb (0 0 1) surfaces prepared by MBE with in situ RHEED and STM. Under fixed  $\text{Sb}_4$  flux, two AlSb reconstructions are observed with increasing temperature (and decreasing surface Sb:Al coverage):  $c(4 \times 4)$  and  $(1 \times 3)$ . In contrast, four different GaSb reconstructions are observed:  $(2 \times 5)$ ,  $(1 \times 5)$ ,  $c(2 \times 6)$ , and  $(1 \times 3)$ . Whereas the  $(1 \times 5)$ ,  $c(2 \times 6)$ , and  $(1 \times 3)$  surfaces are composed primarily of Sb dimer rows on top of an Sb-terminated surface, the  $(2 \times 5)$  surface is composed of Sb dimer rows on top of two layers of Sb, i.e. it is terminated by *three* layers of Sb. We propose that GaSb is unique in forming the  $(n \times 5)$  reconstructions due to its excellent lattice match with trigonally bonded elemental Sb combined with its lower stiffness compared with AlSb.

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